

O 1s XAS of H₂O in the solvation shell of monovalent and trivalent ions

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INTRODUCTION

Earlier experiments with the Soft X-ray Endstation for Environmental Research (SXEER) have shown that pure liquid water consists of three different species of water molecules - symmetric (SYM), acceptor asymmetric (A-ASYM), and donator asymmetric (D-ASYM) [1]. By dissolving Potassium Chloride or Aluminum Chloride we introduce a fourth type of water species - water molecules in the solvation shell of the dissolved ions. X-ray Absorption Spectroscopy at the oxygen K-edge (O 1s XAS) gives the information of Oxygen p-character and hence the local geometric arrangement around the probed oxygen atom. In this report we will show some of the XAS spectra we have obtained at beamline 8.0.

O 1s XAS OF WATER WITH DISSOLVED KCl AND AlCl₃

If we dissolve Potassium Chloride (KCl) into water, the water molecules will form a solvation shell around each Potassium- and Chloride ion. These water molecules will have a different electronic structure than a water molecule in the bulk water. We can actual say that we have a fourth water species. Figure 1 is showing a XAS spectrum at the oxygen edge of water with dissolved KCl. We can see changes in two energy ranges. The pre-edge at 535 eV has higher intensity and has a shoulder at 534.3 eV. This is probably due to changes in the distribution of D-ASYM water species in the bulk water. The higher intensity at 537.0 eV can be explained by water molecules in the solvation shell of K⁺ ion. Preliminary calculations are supporting the experimental data.

Comparing water dissolved KCl with water dissolved Aluminum Chloride (AlCl₃) can give some input to the interpretation. An O 1s XAS spectrum of water with dissolved AlCl₃ is shown in figure 2. As in dissolved KCl there is a shoulder at 534.3 eV. For water with dissolved AlCl₃ the shoulder is more distinct and indicates that the feature at 535 eV is a double peak. However, the interpretation is the same as in the case of dissolved KCl - there are changes in the distribution of D-ASYM water species in the bulk. At higher energy the O 1s XAS spectrum of water with dissolved AlCl₃ is showing higher intensity than pure water. If we compare the spectrum of water dissolved AlCl₃ with water dissolved KCl we can see that water dissolved AlCl₃ have lower intensity at 537.0 eV and higher intensity at 540.5 eV. This can be explained by differences in the electronic structure of water molecules in the solvation shell of trivalent ions from that of monovalent ions. Preliminary calculations show that the fourth water species, water molecules in the solvation shell of the Al³⁺ ion, is giving higher intensity in a different energy range than the water molecules in the solvation shell of the K⁺ ion.

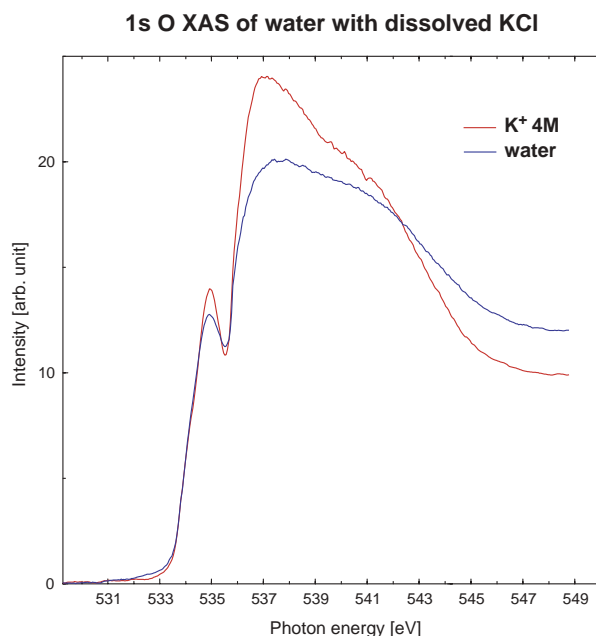


Figure 1. Oxygen 1s XAS of water with dissolved Potassium Chloride (KCl) compared to pure water. The spectrum of water with dissolved KCl has a shoulder at 534.3 eV. It is easier seen in figure 2.

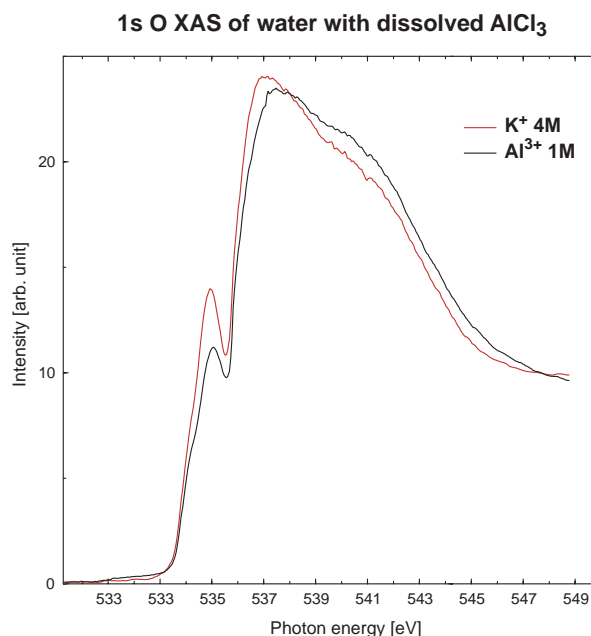


Figure 2. Oxygen 1s XAS of water with dissolved Aluminum Chloride (AlCl_3) compared to water with dissolved Potassium Chloride (KCl).

CONCLUSION

We have shown that O 1s XAS is sensitive enough to resolve the electronic structure of water molecules in a solvation shell of an ion. As an example we have presented differences in the O 1s XAS spectrum between pure liquid water, water with dissolved KCl and water with dissolved AlCl_3 . The distribution of the D-ASYM water species in bulk water is changing when KCl or AlCl_3 is dissolved in the water. Further investigation will tell how the distribution is changed.

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